Appendix 3. Meeting paper AIAA-2008-1209-247

Dissociation cross sections and rate coefficients for nitrogen from accurate theoretical calculations

Galina Chaban[6], Richard Jaffe[7], and David W. Schwenke[8]
NASA Ames Research Center, Moffett Field, CA, 94035-1000, USA

and

Winifred Huo[9]
Huo Consulting, LLC, Los Altos, CA, 94024-3168, USA

The N, N_2 system is studied to yield rate coefficients and cross sections for molecular dissociation under conditions important for assessing nonequilibrium heating of hypersonic vehicles. First principle calculations are used to generate realistic nuclear interaction potentials, and these are used with accurate molecular dynamics to yield the fundamental data required for a rigorous treatment of nonequilibrium chemistry.

Nomenclature

E_{trans}	=	translational energy
g	=	speed
f	=	Boltzmann energy distribution
j	=	rotational quantum number
k_{ab}^{X}	=	rate coefficient for process X labeled by ab
v	=	vibrational quantum number
n_x	=	concentration of species x
ϕ	=	Jacobi coordinate, twist of N_2 molecules about vector connecting N_2 centers of mass
r_1	=	Jacobi coordinate, first NN distance
r_2	=	Jacobi coordinate, second NN distance
R	=	Jacobi coordinate, separation of N_2 centers of mass
σ_{ab}^{X}	=	cross section of type X labeled by ab
θ_1	=	Jacobi coordinate, angle of first NN with respect to vector connecting N_2 centers of mass
θ_2	=	Jacobi coordinate, angle of second NN with respect to vector connecting N_2 centers of mass
T_{trans}	=	translational temperature
t	=	time

I. Introduction

PACE-CRAFT entering planetary atmospheres must withstand significant heating as the aero braking arising from Sthe interaction with the atmosphere converts kinetic energy of the craft into chemical energy. If the entry speed is low enough, e.g. less than about 11 Km/s, which is the entry speed for the space shuttle, the rates of the chemical processes are sufficiently fast that chemical equilibrium is an adequate model to describe the role of chemistry in the flow equations and to model the heating. When chemistry is in equilibrium, the chemical composition and chemical energy is determined by a single parameter, the local temperature.

---

[6] Research Scientist, TNA, T27B-1.
[7] Research Scientist, TSN, 230-3, AIAA Member.
[8] Research Scientist, TNA, T27B-1, AIAA Member.
[9] Principal Scientist, Huo Consulting LLC, 680 Blinn Court, AIAA Member.

When entry speeds increase, the chemical time scales and flow time scales become more similar, and reliable predictions of heating are no longer possible without explicitly dealing with nonequilibrium chemistry. For example, the Stardust return capsule entered the earth's atmosphere at about 12.6 Km/s, and nonequilibrium N_2 dissociation played a significant role in predicting the shock heating. At even higher entry speeds, such as lunar return, nonequilibrium ionization is expected to play an important role. However, in contrast to the equilibrium situation where the local temperature controls everything, a reliable description of nonequilibrium chemistry is much, much more complicated. In the past,[1] the solution to the nonequilibrium chemistry problem has been to build models with additional variables, such specific species concentrations and internal state distribution function parameters. The problem with this solution is that the model can contain many uncertainties that can be extremely difficult to quantify. One often ignored problem is that the phenomenological nature of the model causes the input rate coefficients to lose their physical meaning, thus it is difficult to judge how one relates data obtained from experiments designed to measure rate data to the quantities required for the model. One is then left with validation of the models by comparing to experimental data from laboratory experiments that only approximately mimic flight conditions, or by comparing to the very sparse flight data. In either case, the harsh conditions involved make the interpretation and exact characterization of the data fiendishly difficult and unambiguous model improvement is impossible.

Under the support of the NASA Fundamental Aeronautics Hypersonic research program, the computational chemists at NASA Ames have embarked on an alternate solution, namely the characterization of nonequilibrium chemistry from first principles. The first atmospheric composition we consider is made initially of pure N_2. In future work, we plan to consider a realistic air atmosphere. In this work we will focus our attention on the dissociation of N_2 by means of collisions with N atoms and N_2 molecules.

II. Theoretical Methods

A first principle description of nonequilibrium chemistry can be obtained by the solution of the so-called master equation. In this formulism, we assume that translational degrees of freedom equilibrate instantaneously to a distribution governed by the temperature T_{trans}. See, for example previous work by Schwenke.[2] The translational temperature can be fixed, or driven by coupling to flow equations. The solution then describes the time dependence of the concentrations for the processes

$$\begin{aligned}
&\mathrm{N_2}(j,v) \leftrightarrow 2\mathrm{N} \\
&\mathrm{N_2}(j,v) + \mathrm{N} \leftrightarrow \mathrm{N_2}(j',v') + \mathrm{N} \\
&\mathrm{N_2}(j,v) + \mathrm{N_2}(\bar{j},\bar{v}) \leftrightarrow \mathrm{N_2}(j',v') + \mathrm{N_2}(\bar{j}',\bar{v}') \\
&\mathrm{N_2}(j,v) + \mathrm{N} \leftrightarrow 3\mathrm{N} \\
&\mathrm{N_2}(j,v) + \mathrm{N_2}(\bar{j},\bar{v}) \leftrightarrow \mathrm{N_2}(j',v') + 2\mathrm{N} \\
&\mathrm{N_2}(j,v) + \mathrm{N_2}(\bar{j},\bar{v}) \leftrightarrow 4\mathrm{N}
\end{aligned} \tag{1}$$

for external temperature T_{trans}, where j is the rotational quantum number and v is the vibrational quantum number. The master equation can be written in many forms, and the one we choose for Eq. (1) is

$$\begin{aligned}
-\frac{dn_{jv}}{dt} &= \sum_{j'v'} \left(\tilde{k}^{f}_{j'v' \leftarrow jv} n_{jv} - \tilde{k}^{b}_{jv \leftarrow j'v'} n_{j'v'} \right) - \tilde{k}^{R}_{jv} n_{\mathrm{N}}^2 \\
-\frac{1}{2}\frac{dn_{\mathrm{N}}}{dt} &= \sum_{jv} \left(\tilde{k}^{f}_{jv} n_{\mathrm{N}}^2 - \tilde{k}^{b}_{jv} n_{jv} \right),
\end{aligned} \tag{2}$$

where n_{jv} is the concentration of $N_2(j,v)$, n_{N} is the concentration of N atoms, the sums are over all bound and all long lived metastable levels of N_2, and the $\tilde{k}$ are pseudo first or second order rate coefficients defined as

$$\tilde{k}^{f}_{j'v'\leftarrow jv} = \delta_{j'j}\delta_{v'v}\left[k^{PD}_{jv} + k^{D,\mathrm{N}}_{jv}n_{\mathrm{N}} + \sum_{\bar{j}\bar{v}}\left(1+\delta_{\bar{j}\bar{j}}\delta_{v\bar{v}}\right)k^{DD}_{jv\bar{j}\bar{v}}n_{\bar{j}\bar{v}}\right] + k^{ET,\mathrm{N}}_{j'v'\leftarrow jv}n_{\mathrm{N}}$$
$$+ \sum_{\bar{j}'\bar{v}'\bar{j}\bar{v}}\left(1+\delta_{\bar{j}\bar{j}}\delta_{v\bar{v}}\right)k^{ET,\mathrm{N}_2}_{j'v'\bar{j}'\bar{v}'\leftarrow jv\bar{j}\bar{v}}n_{\bar{j}\bar{v}} + \sum_{\bar{j}\bar{v}}\left(1+\delta_{\bar{j}\bar{j}}\delta_{\bar{v}v}\right)k^{D,\mathrm{N}_2}_{j'v'\leftarrow jv\bar{j}\bar{v}}n_{\bar{j}\bar{v}}, \tag{3}$$

$$\tilde{k}^{b}_{jv\leftarrow j'v'} = k^{ET,\mathrm{N}}_{jv\leftarrow j'v'}n_{\mathrm{N}} + \sum_{\bar{j}'\bar{v}'\bar{j}\bar{v}}\left(1+\delta_{\bar{j}\bar{j}}\delta_{v\bar{v}}\right)k^{ET,\mathrm{N}_2}_{jv\bar{j}\bar{v}\leftarrow j'v'\bar{j}'\bar{v}'}n_{\bar{j}'\bar{v}'} + \sum_{\bar{j}\bar{v}}\left(1+\delta_{\bar{j}\bar{j}}\delta_{v\bar{v}}\right)k^{R,\mathrm{N}_2}_{jv\bar{j}\bar{v}\leftarrow j'v'}n^2_{\mathrm{N}}, \tag{4}$$

$$\tilde{k}^{R}_{jv} = k^{TR}_{jv} + k^{R,\mathrm{N}}_{jv}n_{\mathrm{N}} + \sum_{\bar{j}\bar{v}}\left(1+\delta_{\bar{j}\bar{j}}\delta_{v\bar{v}}\right)k^{DR}_{jv\bar{j}\bar{v}}n^2_{\mathrm{N}}, \tag{5}$$

$$\tilde{k}^{f}_{jv} = k^{TR}_{jv} + \sum_{j'v'\bar{j}\bar{v}}k^{R,\mathrm{N}_2}_{jv\bar{j}\bar{v}\leftarrow j'v'}n_{j'v'} + k^{R,\mathrm{N}}_{jv}n_{\mathrm{N}} + 2\sum_{\bar{j}\bar{v}}k^{DR}_{jv\bar{j}\bar{v}}n^2_{\mathrm{N}}, \tag{6}$$

$$\tilde{k}^{b}_{jv} = k^{PD}_{jv} + k^{D,\mathrm{N}}_{jv}n_{\mathrm{N}} + \sum_{j'v'\bar{j}\bar{v}}k^{D,\mathrm{N}_2}_{j'v'\leftarrow jv\bar{j}\bar{v}}n_{\bar{j}\bar{v}} + 2\sum_{\bar{j}\bar{v}}k^{DD}_{jv\bar{j}\bar{v}}n_{\bar{j}\bar{v}}, \tag{7}$$

where δ_{nm} is unity if n=m and zero otherwise, k^{ET} is an energy transfer rate coefficient, k^{D} is an dissociation rate coefficient, k^{R} is an recombination rate coefficient, k^{PD} is a predissociation rate coefficient, k^{TR} is a tunneling recombination rate coefficient, k^{DD} is a double dissociation rate coefficient, and k^{DR} is a double recombination rate coefficient. The predissociation and tunneling recombination rate coefficients are nonzero only for metastable jv levels. For the N_2 molecule, there are thousands of possible jv levels, so the solution of the master equation will be very arduous.

The rate coefficients depend on T_{trans} through the relation

$$k^{X}_{ab} = \int_0^\infty g(E_{trans})\sigma^{X}_{ab}(E_{trans})f(E_{trans},T_{trans})dE_{trans}, \tag{8}$$

where X is *ET*, *D*, *R*, *PD*, *TR*, *DD*, or *DR*, *ab* is one of the appropriate set of indices, g is the speed at translational energy E_{trans}, σ^{X}_{ab} is the cross section for the process *ab* of type X at E_{trans}, and f is the normalized Boltzmann energy distribution at temperature T_{trans}. The predissociation rate is independent of E_{trans} and T_{trans}, and the tunneling recombination rate is computed from the predissociation rate and microscopic reversibility.

Thus the fundamental quantity required for master equation simulations at any translational temperature are the cross sections σ^{X}_{ab}. In some cases these can be determined experimentally, but it is much more practical and reliable to determine these also from calculations. To do this, we must solve for the motion of the electrons and nuclei for a system of 3 or 4 N atoms. This is carried out by a three step process: (i) carry out electronic structure calculations to optimize the electronic energy for a set of well chosen fixed nuclear positions, (ii) determine an interpolation/extrapolation function that well represents the results of the electronic structure calculations, and (iii) solve for the nuclear dynamics to determine the cross sections. The result of step (ii) is customarily called the potential energy surface (PES).

The PES for N_2+N had been studied previously.[3] The PES used for 3N in the present work is an extension of that surface. The previous surface had two draw backs: first it was based on electronic energies determined using wave function parameters from the restricted open-shell coupled-cluster-single-double method and the fifth order accurate triples energy functional [RCCSD(T) method],[4] and that method breaks down when N_2 bond lengths become large, which is the case when N_2 dissociates. Secondly, the functional form used to interpolate and extrapolate did not behave properly when N_2 dissociated. In the present work we corrected both deficiencies. We ended up discarding the RCCSD(T) energies in favor of ones determined using electronic structure methods based on multi-reference energy functionals that did not break down at dissociated geometries. We ended up using electronic energies at 1344

geometries in the final PES. We discarded the RCCSD(T) energies because we found that the breakdown of the RCCSD(T) energies was very erratic, and we were never sure when they were reliable. The functional form used in the new PES was the same as in our previous work except the badly behaved term was corrected, and we used a N_2 potential that was more precise at very large bond lengths. Finally, after the fit to the electronic energies was completed, we replaced our calculated N_2 potential with the best potential based an experimental data.[5] This helps to remove some of the inaccuracies in the computed electronic energies. Further details of this PES will be given elsewhere, but none of the features of the previous PES have changed significantly.

The PES for 4N used in the present work is based on ideas presented previously for 4H.[6] We partitioned the nuclear positions into situations where both N_2 molecules had bond lengths near equilibrium, situations where only one of the N_2 molecules had bond lengths near equilibrium, and other geometries. In the first region, we carried out electronic structure calculations using the closed-shell coupled-cluster-single-double method to parameterize the wave function and the fifth order accurate triples energy functional [CCSD(T) method].[7,8] The CCSD(T) calculations require about 30 minutes of central processor unit (CPU) time per geometry on the NAS facility Columbia computer. This method is much more robust for N_2+N_2 than the RCCSD(T) method was for N_2+N, nonetheless we had difficulty in accessing the reliability of the calculations at many geometries. We ended up using 1271 nuclear geometries in this region. In the second region, we carried out electronic structure calculations using the multi-reference averaged-coupled-pair-function (ACPF) method.[9] Because of the expense of the ACPF calculations, we simplified the calculations by not correlating the 2s like electrons. If the 2s like electrons would be correlated, we estimate that the CPU time would be 10 days per geometry. Not correlating the 2s like electrons reduces the CPU time requirements by about an order of magnitude. Test calculations on the N_2 potential curve showed that this approximation did not significantly impact the accuracy. We used results at 306 nuclear geometries using the ACPF method. To place the ACPF and CCSD(T) calculations on the same footing, we relied heavily on the N_2 potential curves computed using both methods. Finally we assumed that the region where neither N_2 molecules has bond lengths near equlibrium was less important, so we relied on extrapolations of our PES to describe that region.

When attempting to fit the ACPF calculations, it became apparent that there was unexpected structure in the

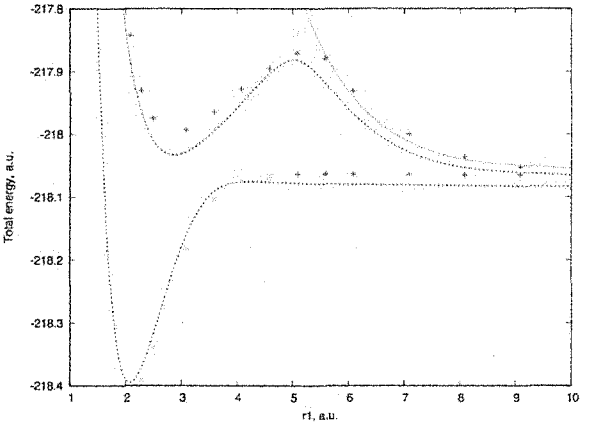

Figure 1. N_4 PES in cross configuration. Symbols, ACPF calculations, dark blue lines, full fit, light blue line, T_d N_4 diabat, purple line, N_2+N+N diabat.

calculated energies. Analysis showed that these were due to local minima in the N_4 potential energy surface, specifically the tetrahedral (T_d) N_4 minimum and the rectangular N_4 minimum. Thus our preliminary PES was taken to be the lowest eigenvalue of a 4×4 matrix, with the 4 electronic states being N_2+N_2 like, N_2+N+N like, T_d N_4 like, and rectangular N_4 like. In fig. 1, we show an example showing the structure. This is for N_4 in the so called cross configuration. The geometries shown in this figure can be most easily specified by the Jacobi coordinates $R,r_1,r_2,\theta_1,\theta_2$, and ϕ. In the cross configuration, $\theta_1=\theta_2=\phi=90^\circ$. In this figure r_2 is fixed at the equilibrium separation of 2.08 a.u., and R is 2 a.u. or 5 a.u. The highest set of curves, which are for R=2 a.u., we see the expected repulsion at large r_1, but then the energy has a minimum coming from the T_d N_4, while the N_2+N+N and N_2+N_2 like diabats are

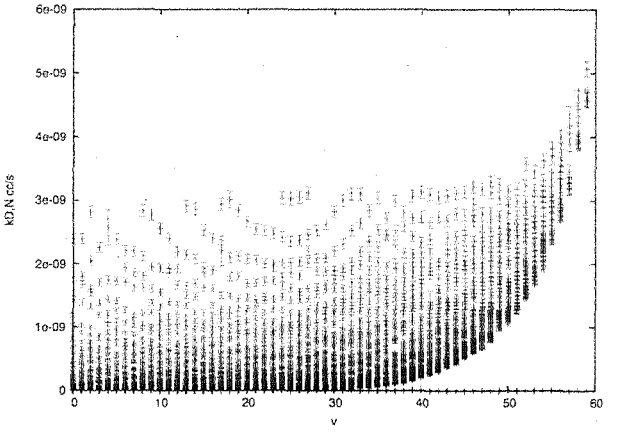

Figure 2. Dissociation rate coefficients at T_{trans}=10,000K.

much higher in energy. At the lower curve, which is for R=5 a.u., we only see the influence of the N_2+N+N and N_2+N_2 diabats. These features introduce significant additional complications into the analytic representation of the PES. The analytic representation in the vicinity of the tetrahedral minimum was based on the frequencies and relative energies reported by Lee.[10] In the region of the rectangular local minima, we carried out calculations at 467 geometries using the CCSD(T) method to constrain the analytic representation. Both the T_d and rectangular local minima are about 50 kcal/mol (0.08 a.u.) below N_2+N+N, so scrambling of the N atoms will be possible before dissociation takes place. The PES treats all N atoms equivalently and reproduces the 3N PES used in this work when one N is pulled away. In further work we will give the full details of this PES.

In our previous work on N_2+N,[3] the nuclear dynamics calculations were carried out by quantum mechanical (QM) calculations. In the present work, the nuclear dynamics calculations were carried out by means of the quasi-classical trajectory (QCT) method. This was done for several reasons. First of all was the expense of the QM calculations and the difficulty in treating dissociation. The second was that the regime where the QM calculations is expected to have the most difficulty is also the regime where the QCT method is expected to be most accurate. Finally, the QCT method has no difficulty in treating molecular dissociation. Recombination cross sections are determined via microscopic reversibility.

The nuclear dynamics calculations were carried out using the code used previously for H_2+H and H_2+H_2.[6] We used stratified sampling for the impact parameter to maximize the accuracy of both large and small cross sections. In

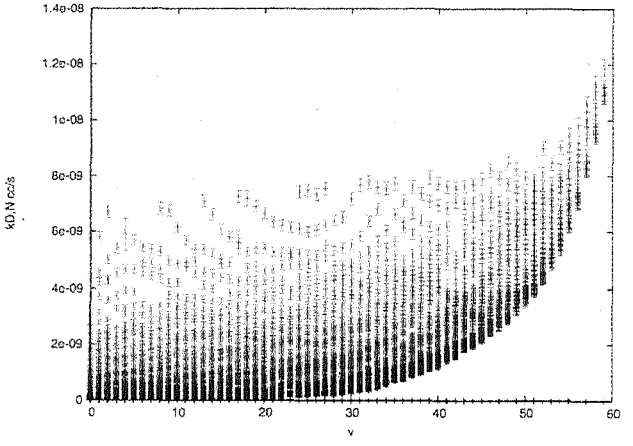

Figure 3. Dissociation rate coefficients at T_{trans}=20,000K.

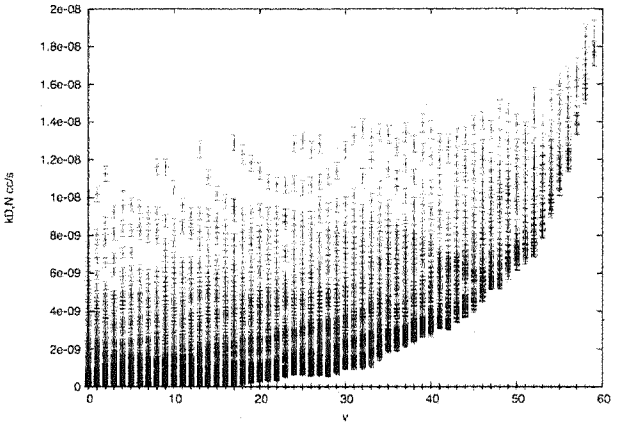

Figure 4. Dissociation rate coefficients at T_{trans}=30,000K.

our previous work,[6] the integral in Eq. (8) was carried out by Monte-Carlo sampling along with the weighted averaging over the other unspecified initial conditions. Thus energy dependent cross sections were not reported. In the present work on $N+N_2$, we will give energy dependent cross sections by means of the following procedure. For each initial *jv* state, we carried out two batches of trajectories. The first batch, consisting of 6000 trajectories, used Monte-Carlo sampling of E_{trans} using T_{trans}=20,000K. In the second batch, we ran 600 trajectories, and sampled E_{trans} using T_{trans}=60,000K. We then divided E_{trans} into bins and interpreted the average cross section computed for all trajectories with energies lying in a particular bin to represent the cross section averaged over the energy in that bin. The distinction between the two is quite subtle and relates to an unbiased estimation of the error of the approximation. For high energy bins, the number of trajectories with energies falling into them was small, and consequently the Monte-Carlo statistics are very poor. Nonetheless the size of the Boltzmann factor at high energy should ensure these poor statistics will have no consequence in simulations of realistic re-entry conditions. Typically, about 8 CPU hours were required for the calculations for each *jv* level.

III. Results and discussion

For N_2, there are 9390 bound or long lived metastable levels determined using the primitive WKB method.[6] There are levels with *j* up to 279 and *v* up to 60. The coupling between *v* and *j* is explicitly included in all calculations. For $N+N_2$ over 60 million trajectories were run. For N_2+N_2, our PES is still undergoing refinement, so only a small number of trajectories were run. It is difficult to digest all the data generated by these calculations, and we will present the data in several forms. A figure showing all the dissociation cross sections as a function of E_{trans} is shown in the nano dot at the end of this sentence.

What energy ranges, or temperatures are important for simulations of hypersonic entry conditions? It is hard to tell with certainty. Estimates from computational-fluid-dynamics (CFD) calculations on vehicles such as Stardust yield peak temperatures in the vicinity of 20,000K,[11] but direct-simulation-Monte-Carlo (DSMC) calculations show much higher temperatures: circa 80,000K.[11] Nonetheless we focused our calculations most strongly at 20,000K.

In figs. 2-4 we show the dissociation rate coefficients for $N+N_2$ for all jv levels for T_{trans}=10,000K, 20,000K, and 30,000K. On the whole, the results at the different temperatures look similar, apart from the increase as the temperature increases. The plots show confusing families of curves with rate coefficients with different values of j. Thus vibrational-rotational coupling is clearly extremely important. We have tried correlating the rate coefficients with other variables, such as the height of the centrifugal barrier needed for dissociation relative to the vibrational level, but a simple relation does not appear to exist. Another observation is as the temperature goes up, so does the minimum v where the rate constants become significantly different from zero. There also is some interesting structure that develops at the bottom edge of the plot as T_{trans} becomes higher. The source of this structure is unknown, but may be due to the worse statistics at the higher temperatures because fewer trajectories were run.

Now some of the largest rate coefficients occur for the highest values of v. We expect that if some sort of Boltzmann population existed for vibration, then the highest values of v would likely have very small populations. Thus we also plot the dissociation rate coefficients multiplied by the Boltzmann probability for each jv level. This is show in figs. 5 and 6 for the case T_{trans}=20,000K where we also use T_{trans} to compute the probabilities for populating the levels. We find that there are many levels which have large equilibrium one way dissociation fluxes, but the level with the largest flux is the one with jv=270,2. Since our 4N PES is still in the final stages of optimization, we will only run trajectories for this jv at T_{trans}=20,000K, and $\overline{jv}$=59,0, which is the most likely level at this T_{trans}. At press time, we had not completed enough trajectories to give meaningful statistics, so these results will be reported elsewhere.

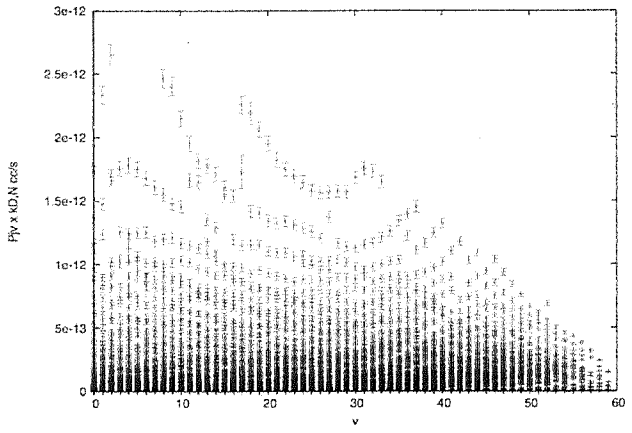

Figure 5. Dissociation rate coefficients times population probabilities.

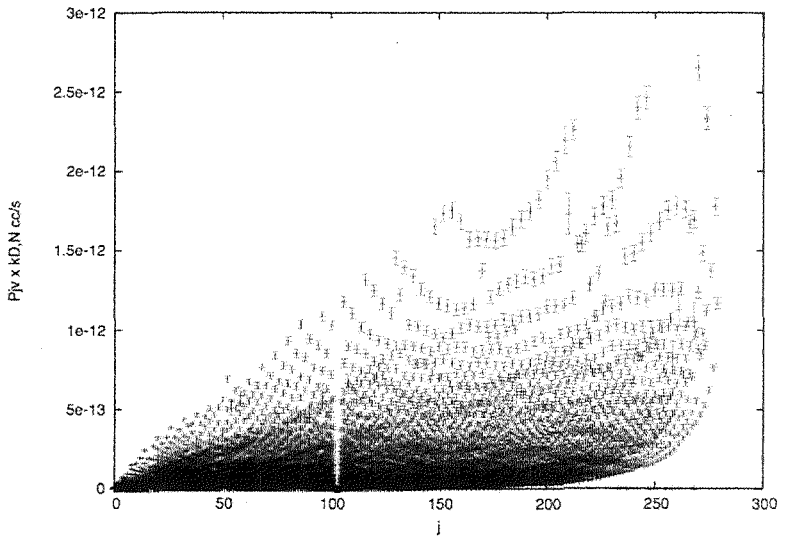

Figure 6. Dissociation rate coefficients times population probabilities.

IV. Conclusions

We have carried out reliable first principle calculations of dissociation cross sections for $N+N_2$ for all 9390 *jv* levels. Our PES predicts large cross sections for levels with very large *j*. Our PES for N_2+N_2 reflects the complex features in the system, including fairly strongly bound local minima which will give rise to very interesting dynamics when the scattering energy is large enough to cause dissociation. Once we finish our calculations of the cross sections for N_2+N_2, we will perform solutions of the master equation and model accurately for the first time the nonequilibrium dissociation of N_2 in hypersonic entry

Acknowledgments

The work of W. Huo is funded by NASA/ARMD Fundamental Aeronautics/Hypersonics Program contract # NNA07BA89C.

References

[1]Park, C, *Nonequilibrium Hypersonic Aerothermodynamics*, Wiley, New York, 1990.

[2]Schwenke, D. W., "A theoretical prediction of hydrogen molecule dissociation-recombination rates including an accurate treatment of internal state nonequilibrium effects," *J. Chem. Phys.*, Vol. 92, No. 8, 1990, pp. 7267-7282.

[3]Wang, D., Stallcop, J. R., Huo, W. M., Dateo, C. E., Schwenke, D. W., and Partridge, H., "Quantal Study of the Exchange Reaction for $N+N_2$ using an *ab initio* potential energy surface," *J. Chem. Phys.*, Vol. 118, No. 3, 2003, pp. 2186-2189.

[4]Knowles, P. J., Hampel, C., and Werner, H.-J.,"Coupled cluster theory for high spin, open shell reference wave functions," *J. Chem. Phys.*, Vol. 99, No. 7, 1993, pp. 5219-5227.

[5]LeRoy, R. J., Huang, Y., and Jary, C.,"An accurate analytic potential function for ground-state N_2 from a direct-potential-fit analysis of spectroscopic data," *J. Chem. Phys.*, Vol. 125, 2006, pp. 165410

[6]Schwenke, D. W., "Calculation of rate constants for the three-body recombination of H_2 in the presence of H_2," *J. Chem. Phys.*, Vol. 89, No. 2, 1988, pp. 2076-2091.

[7]Purvis, G. D., and Bartlett, R. J., "A Full Coupled-cluster Singles and Doubles Model: The Inclusion of Disconnected Triples," *J. Chem. Phys.*, Vol. 76, No. 2 ,1982, pp. 1910-1918.

[8]Raghavachari, K., Trucks, G. W., Pople, J. A., and Head-Gordon, M., "A Fifth-order Perturbation Comparison of Electron Correlation Theories," *Chem. Phys. Lett.*, Vol. 157, No. 5, 1989, pp. 479-483.

[9]Gdanitz, R. J. and Ahlrichs, R. "The averaged coupled-pair functional (ACPF): A size-extensive modification of MR CI(SD)," *Chem. Phys. Lett.*,Vol. 143, No. 4, 1988, pp. 413-420.

[10]Lee, T.J. and Martin, J. M. L., "An accurate quartic force field, fundamental frequencies, and binding energy for the high energy density material T_dN_4," *Chem. Phys. Lett.*, Vol. 357, No. 4, 2002, pp. 319-325.

[11]Boyd, I., personal communication.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.			
1. REPORT DATE (DD-MM-YYYY) 18-01-2008	2. REPORT TYPE Quarterly		3. DATES COVERED (From - To) October 1, 2007 - December 31, 2007
4. TITLE AND SUBTITLE Chemical reaction and electron-impact excitation rates for direct numerical simulations and radiation transport modeling in the hypersonic regime			5a. CONTRACT NUMBER NNA07BA89C 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Winifred Huo			5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Huo Consulting LLC 680 Blinn Court Los Altos, CA 94024-3168			8. PERFORMING ORGANIZATION REPORT NUMBER Huo2008Q1
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) NASA Ames Research Center Contract specialist: Janessa M. Langford, Mail Stop 241-1 Technical Monitor: Nagi Mansour, Mail Stop 230-2 Moffett Field, CA 94035-1000			10. SPONSORING/MONITOR'S ACRONYM(S) ARC 11. SPONSORING/MONITORING REPORT NUMBER
12. DISTRIBUTION/AVAILABILITY STATEMENT Publicly available STI			
13. SUPPLEMENTARY NOTES			
14. ABSTRACT Electron impact ionization cross sections/rate coefficients of ground state O atom have been calculated. Comparison with available experimental cross section data leads to an estimated uncertainty of 15%. The radiative recombination of N+ and O+ with electrons producing dipole radiation has been successfully studied. It demonstrates the importance of the VUV radiation from this process.			
15. SUBJECT TERMS Electron-impact ionization of O atom and radiative recombination of N+ and O+ with electrons			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT	b. ABSTRACT	c. THIS PAGE	
			SAR
18. NUMBER OF PAGES 45	19b. NAME OF RESPONSIBLE PERSON Winifred Huo 19b. TELEPHONE NUMBER (Include area code) (650) 968-7805		

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18